CLAIMS

1. A method of preparing a porphyrin derivative starting from a meso-substituted porphyrin compound, **characterized** in that a meso-(2'-cyanovinyl)-substituted porphyrin compound of which the vinyl is optionally substituted is used as the meso-substituted porphyrin compound, wherein said meso-(2'-cyanovinyl)-substituted porphyrin compound, in a form in which its porphyrin macrocycle is complexed with a bivalent metal ion

i) is subjected to

an acid for which $0 < pKa < 5$

and

an oxidising agent,

with the restriction that if the carbon atom of the porphyrin macrocycle at which the (2'-cyanovinyl) substituent is attached is designated Cα, there must be a substituent attached to Cδ, counting along the perimeter of the porphyrin macrocycle, said substituent comprising a -C-C motif directly attached at the Cδ carbon atom;

or

ii) is subjected under aprotic conditions to a Vilsmeier reagent having a reactive motif

$$C^2 - N = C^3 \quad (C^1 \text{ attached to } C^2)$$

containing a quaternary nitrogen atom which is directly linked to two carbon atoms C^1, C^2 wherein said carbon atoms are not part of a unsaturated or aromatic moiety, and which quaternary nitrogen atom is directly linked to a carbon atom C^3 via a double bond, said carbon atom C^3 carrying a halogen atom chosen from fluoro, chloro, bromo and iodo

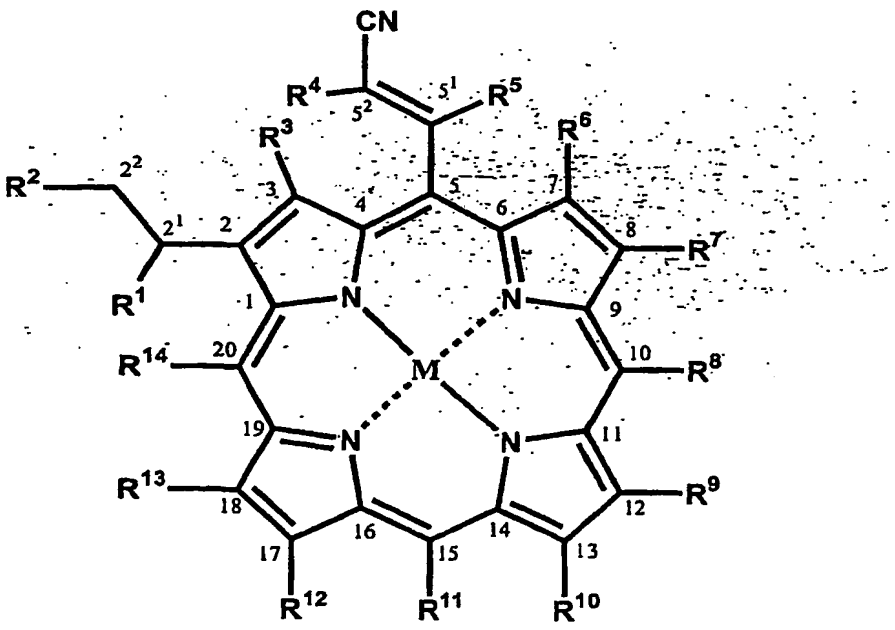
with the restriction that if the carbon atom of the porphyrin macrocycle at which the (2'-cyanovinyl) substituent is attached is designated Cα, there must be a sub-

stituent attached to Cδ, counting along the perimeter of the porphyrin macrocycle, said substituent comprising a -CH motif directly attached at the Cδ carbon atom;

to convert said meso-(2'-cyanovinyl)-substituted porphyrin compound into a porphyrin derivative having a quinoline-ring system peri-condensed to the porphyrin ring, and optionally the bivalent metal ion is removed or replaced by another metal ion, and optionally the nitrogen atom of the quinoline-ring system ring is quaternized.

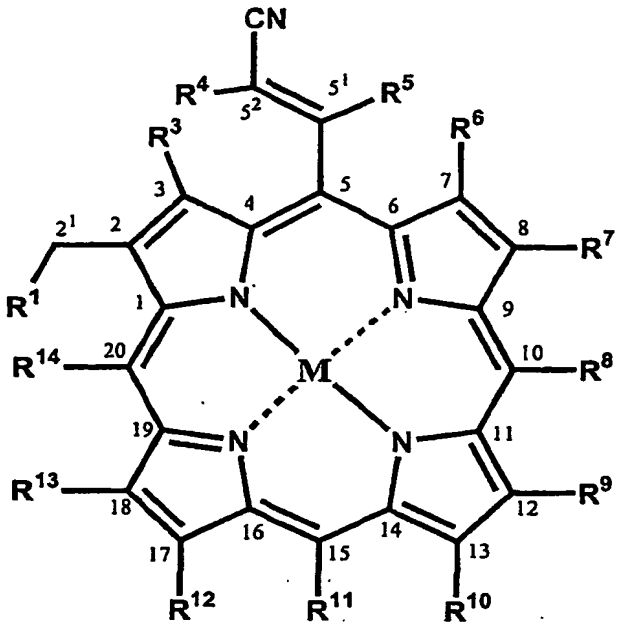
2. The method according to claim 1, **characterized** in that for alternative step i) a meso-(2'-cyanovinyl)-substituted porphyrin compound of formula (I) is used as the starting compound,

(I)



or wherein for alternative step ii) meso-(2'-cyanovinyl)-substituted porphyrin compound of formula (III) is used as the starting compound

(III)



wherein

R^1, R^2 represent independently of each other hydrogen, linear or branched (C_{1-8}) alkyl, or linear or branched (C_{1-8})alkyl C(O)O (C_{1-8})alkyl, wherein the groups comprising alkyl may optionally be substituted with fluoro, chloro, bromo, iodo, nitrile, (C_{1-8}) thioether, and (C_{1-8}) alkoxy;

R^3 represents H or (C_{1-8}) alkyl;

R^4 and R^5, represent, independently of each other, hydrogen, nitrile, monocyclic, bicyclic or tricyclic (C_{6-14}) aryl, or (C_{1-4}) alkyl wherein the aryl and alkyl group may optionally be substituted with fluoro, chloro, bromo, iodo, nitrile, (C_{1-8}) thioether, and (C_{1-8}) alkoxy;

R^6 to R^{14} represent independently of each other, hydrogen, linear or branched (C_{1-8}) alkyl, linear or branched (C_{1-8})alkyl C(O)O (C_{1-8})alkyl, wherein n is an integer of 0 to 4, CH_2=CH-, a monocyclic, bicyclic or tricyclic (C_3-C_{14}) aryl, which aryl may optionally contain one or more nitrogen atoms as heteroatoms; and R^8, R^{11}, and R^{14} may in addition represent an acrylonitrile group substituted with $R^{4'}$ and $R^{5'}$, wherein

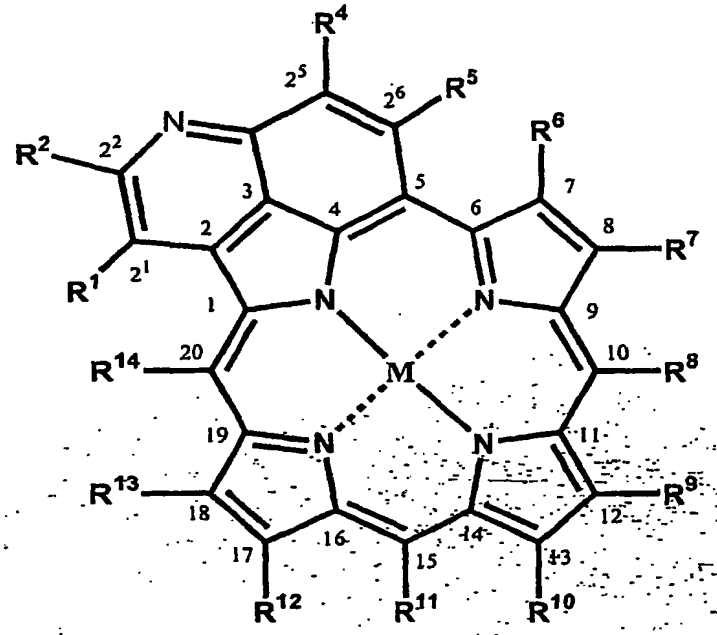
$R^{4'}$ and $R^{5'}$ are as defined for R^4 and R^5;

and

M represents a bivalent metal ion,

wherein the compound of formula (I) or (III) is converted into the corresponding porphyrin derivative of formula (II) comprising a quinoline-ring system fused to the porphyrin ring

(II)



wherein the substituents have the meanings given above, and depending on the meaning of R^8, R^{11}, and R^{14} and the correspondence of an adjacent R^7, R^9, R^{10}, R^{12}, and R^{13} with R^3 optionally more than one quinoline-ring system peri-condensed to the porphyrin ring is present.

3. The method according to claim 1 or 2, **characterized** in that the nitrogen atom of the peri-condensed quinoline-ring system ring in formula (II) is quaternized.

4. The method according to any of the preceding claims, **characterized** in that the meso-(2'-cyanovinyl)-substituted porphyrin compound is prepared by introducing a formyl or acetyl residue at a meso position of a porphyrin compound, whereafter the mesoformylporphyrin thus formed is converted

into the meso-(2'-cyanovinyl) derivative.

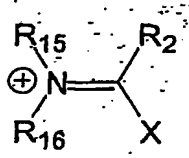
5. The method according to claim 4, **characterized** in that the mesoformylporphyrin formed is converted into the meso-(2'-cyanovinyl)-substituted porphyrin compound by reaction with diethylphosphonoacetonitril.

6. The method according to any of the preceding claims, **characterized** in that the porphyrin starting compound for the preparation of the meso-(2'-cyanovinyl) porphyrin is chosen from the group of i) hemin, and ii) heme.

7. The method according to any of the preceding claims, **characterized** in that Ni^{2+} is used as the bivalent metal ion.

8. The method according to any of the preceding claims, **characterized** in that a Brönsted-acid is used with the provisio that $0 < pKa < 5$, the reaction being carried out at a temperature above 140°C.

9. The method according to any of the claims 1 to 7, **characterized** in that the Vilsmeier reagent used is of the formula (IV)



(IV)

wherein

R15 and R16 are, independently of each other, linear or branched C_{1-8} alkyl,

X is fluoro, chloro, bromo and iodo, and

R2 is hydrogen, linear or branched (C_{1-8}) alkyl, or linear or branched (C_{1-8})alkyl C(O)O (C_{1-8})alkyl, wherein the groups comprising alkyl may optionally be substituted with fluoro, chloro, bromo, iodo, nitrile, (C_{1-8}) thioether, and (C_{1-8}) alkoxy.

10. The method according to claim 9, **characterized** in that X is chloro or bromo.

11. Porphyrin derivatives, wherein said derivatives are:

- 2'-methoxycarbonylquino[4,4a,5,6-jkl]-annulated 12-demethyl-13-de[2-(methoxycarbonyl)ethyl]mesoporphyrin dimethylester;
- 2'-methoxycarbonylquino[4,4a,5,6-qrs]-annulated 18-demethyl-17-de[2-(methoxycarbonyl)ethyl]mesoporphyrin dimethylester;
- quino[4,4a,5,6-abt]-annulated 2-demethyl-3-deethylmesoporphyrin dimethylester;
- quino[4,4a,5,6-efg]-annulated 7-demethyl-8-deethylmesoporphyrin;
- 2'-methoxycarbonylquino[4,4a,5,6-jkl]-annulated 12-demethyl-13-de[2-(methoxycarbonyl)ethyl]mesoporphyrin;
- 2'-methoxycarbonylquino[4,4a,5,6-qrs]-annulated 18-demethyl-17-de[2-(methoxycarbonyl)ethyl]mesoporphyrin;
- quino[4,4a,5,6-abt]-annulated 2-demethyl-3-deethylmesoporphyrin;
- quino[4,4a,5,6-bcd]-2-demethyl-3-deethyl-mesoporphyrin dimethylester;
- quino[4,4a,5,6-bcd]-2-demethyl-3-deethyl-mesoporphyrin;
- 3'-methylquino[4,4a,5,6-efg]-7-demethyl-8-deethylmesoporphyrin dimethylester;
- 3'-methylquino[4,4a,5,6-efg]-7-demethyl-8-deethylmesoporphyrin;
- 9'-aminocarbonylquino[4,4a,5,6-efg]-7-demethyl-8-deethylquinoporphyrin dimethylester;
- 9'-aminocarbonylquino[4,4a,5,6-efg]-7-demethyl-8-deethylquinoporphyrin
- N-benzylquinolinium[4,4a,5,6-efg]-annulated mesoporphyrin dimethylester
- N-benzylquinolinium[4,4a,5,6-efg]-annulated mesoporphyrin.

12. A porhyrin derivative having a quinoline-ring system peri-condensed to the porphyrin ring.

13. Use of a porphyrin derivative according to claim 12 for the preparation of a pharmaceutical composition of a porphyrin derivative according to the invention for prevention of and/or treating

1) benign, malignant, inflamed and infectious skin and mucosa disorders: skin/mucosa disorders;

2) vascular disorders;

3) tumors and pre-cancerous lesions;

4) ophthalmology disorders;

5) gynecological or urological disorders;

6) immunological disorders;

7) oral cavity or nasopharyngeal disorders.

14. Use of a porphyrin derivative according to claim 12 for the preparation of a composition of a porphyrin derivative according to the invention for the preparation of a composition

1) for photodetection of malignant and pre-malignant lesions;

2) for decontamination or pathogen reduction of liquids such biological fluids and contaminated water;

3) for decontamination or pathogen reduction of surfaces;

4) for use as insecticide.

15. Pharmaceutical composition comprising a porphyrin derivative according to claim 12 together with a pharmaceutically acceptable carrier or excipient.